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Silicone elastomers with high dielectric permittivity and high dielectric breakdown strength based on tunable functionalized copolymers

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ABSTRACT

High driving voltages currently limit the commercial potential of dielectric elastomers (DEs). One method used to lower driving voltage is to increase dielectric permittivity of the elastomer. A novel silicone elastomer system with high dielectric permittivity was prepared through the synthesis of siloxane copolymers, thereby allowing for the attachment of high dielectric permittivity molecules through copper-catalyzed azide-alkyne 1,3-dipolar cycloaddition (CuAAC). The synthesized copolymers allow for a high degree of chemical freedom, as several parameters can be varied during the preparation phase. Thus, the space between the functional groups can be varied, by using different dimethylsiloxane spacer units between the dipolar molecules. Furthermore, the degree of functionalization can be varied accurately by changing the feed of dipolar molecules. As a result, a completely tunable elastomer system, with respect to functionalization, is achieved. It is investigated how the different functionalization variables affect essential DE properties, including dielectric permittivity, dielectric loss, elastic modulus and dielectric breakdown strength, and the optimal degree of chemical functionalization, where these important properties are not significantly compromised, is also determined. Thus, the best overall properties were obtained for a silicone elastomer prepared with 5.6 wt% of the dipolar molecule 1-ethynyl-4-nitrobenzene. Here, a high increase in dielectric permittivity (~70%) was obtained without compromising other vital DE properties such as elastic modulus, gel fraction, dielectric and viscous loss and electrical breakdown strength.

Keywords: Dielectric elastomer, dielectric constant, permittivity, breakdown, silicone, CuAAC, click reaction
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1. INTRODUCTION

Certain issues currently limit the commercial potential of dielectric elastomers (DEs), including high driving voltages (several kVs) and short device lifetime. Consequently, there is a need to optimize DE materials, in order to overcome the current limitations of the technology. One of the most important components of a DE is the elastomer, as it governs dielectric permittivity and the breakdown strength of the DE. The elastomer, therefore, defines the achievable strain at a given voltage and the maximum possible voltage that can be applied to the DE. Polydimethylsiloxane (PDMS) elastomers are one of the most used materials for DEs, due to their high efficiency, fast response, broad temperature operating range and low viscous losses, which means that the elastomer can be operated at higher frequencies but with lower losses compared to acrylics and polyurethanes[1,2]. The major disadvantage of silicone elastomers is that they possess relatively low dielectric permittivity, compared to acrylics and polyurethanes, which means that a higher electrical field is necessary to obtain a certain strain. A higher strain at a given voltage can be obtained by increasing the energy density of the elastomer, which can be done by creating elastomers with higher dielectric permittivity, i.e. with a higher ability be internally polarized.

Various techniques have been employed to increase dielectric permittivity of silicone elastomers, most commonly the use of metal oxide fillers such as TiO_2[3-8], $BaTiO_3$[8-10], and Al_2O_3[8]. A number of conducting fillers have also been employed, such as expanded graphite[11], carbon nanotubes[12,13], a copper-phthalocyanine oligomer[14,15], and calcium copper titanate ($CaCuTi_4O_{12}$)[16]. Despite increased dielectric permittivity, such composite systems exhibit drawbacks such as large dielectric losses, reduced breakdown strengths and significantly increased Young's moduli (which reduces achievable strain). Several systems have been developed in order to overcome the problems associated with stiff filler materials, including the preparation of encapsulated polyaniline (PANI) particles with insulating polymeric shells that prevent the agglomeration of the PANI particles[17] and blends of PDMS/poly(hexylthiophene)[18] and PDMS/polyethylene

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glycol[19] have been developed to increase homogeneity between the matrix (PDMS) and filler (high dielectric permittivity polymer) and to maintain suitable elastic moduli. An alternative method is to chemically graft organic dipolar molecules to the silicone elastomer network. This approach potentially leads to a more controlled network structure, as it does not rely on the efficient and perfect mixing of particles or blends and should furthermore provide a more stable elastomer system upon continued actuation of the material[20]. A number of schemes has been developed with this approach in mind: Kussmaul et al.[21] and Risse et al.[22] added the synthesized dipolar molecule *N*-allyl-*N*-methyl-*p*-nitroaniline, together with compensating amounts of a hydride-functional cross-linker, to a PDMS matrix and a commercial silicone elastomer system, respectively, in one-step processes. Madsen el al.[23,24] developed a new silicone-compatible cross-linker that allowed for specific functionalization with high dipole moment molecules at the cross-linking point of silicone networks. This was done using a copper-catalyzed azide-alkyne 1,3-dipolar cycloaddition (CuAAC) reaction, which is orthogonal, so that functionality could be added without compromising the network-forming reaction. Racles et al.[25] used another approach where cyanopropyl-groups were distributed along the backbone of PDMS chains. Good overall results were obtained for blends of the cyanopropyl-functional PDMS and PDMS.

High dielectric permittivity silicone elastomers were obtained by these grafting methods, as two-fold increases were usually achieved. When developing such chemically modified elastomer systems it is, however, important to keep in mind other properties that govern the lifetime of the DE, such as dielectric loss, dielectric breakdown strength and the elastic modulus (Young's modulus) as these essential DE properties are easily compromised upon chemical manipulation of the silicone elastomer.

The present work, therefore, aims at developing a new silicone elastomer system with high dielectric permittivity, while maintaining equitable levels of other important elastomer properties such as viscous and dielectric losses and electrical breakdown strengths. The work is based on a new and controlled silicone elastomer system based on functionalizable siloxane copolymers that allow for the attachment of high dipole moment molecules through CuAAC reactions. The copolymers allow for a high degree of chemical freedom, as several parameters can be varied during the preparation phase: the space between the functional groups can be varied, by using different dimethylsiloxane spacer units between the functional dipolar groups and furthermore, the degree of functionalization can be varied accurately by changing the feed of the dipolar molecules. As a result, a completely tunable elastomer system, with respect to functionalization, is achieved. We herein investigate how the different functionalization variables affect essential DE properties, including dielectric permittivity, dielectric loss, elastic modulus and dielectric breakdown strength and thereby determine the optimal degree of chemical functionalization where increased dielectric permittivity are matched with good overall elastomer properties.

2. EXPERIMENTAL

2.1 Materials and methods

Hydride-terminated PDMS, DMS-H11 ($\bar{M}_w \approx 1200$ g mol^{-1} as determined by ^{1}H-NMR), 3-(chloropropyl)methyldimethoxysilane, allyldimethylsilane and a hydride-functional cross-linker, HMS-301, were acquired from Gelest Inc. The platinum cyclovinylmethyl siloxane complex catalyst (511) was purchased from Hanse Chemie. Hydride-terminated PDMS ($\bar{M}_w \approx 580$ g mol^{-1} as stated by supplier) and vinyl-terminated PDMS ($\bar{M}_w$ = 25,000 g mol^{-1} as stated by supplier) were purchased from Sigma-Aldrich. Silicon dioxide amorphous hexamethyldisilazane-treated particles (SIS6962.0) were purchased from Fluorochem. All other chemicals were acquired from Sigma-Aldrich and used as received, unless otherwise stated.

FTIR was conducted on a PerkinElmer Spectrum One model 2000 Fourier Transform Infrared apparatus equipped with a universal attenuated total reflection accessory on a ZnSe/diamond composite. Spectra were recorded in the range of 4000-650 cm^{-1} with 4 cm^{-1} resolution and 16 scans. ^{1}H- and ^{13}C-NMR experiments were performed on a Bruker 300 MHz spectrometer in $CDCl_3$. Size-exclusion chromatography (SEC) was performed on a Tosoh EcoSEC HLC-8320GPC instrument equipped with RI and UV detectors and SDV Linear S columns from PSS. Samples were run in toluene at 35°C at a rate of 1 mL min^{-1}, and molar mass characteristics were calculated using WinGPC Unity 7.4.0 software and linear polydimethylsiloxane (PDMS) standards acquired from PSS. Differential scanning calorimetry (DSC) measurements were performed on a DSCQ1000 from TA Instruments. Mechanical characterization of the prepared films was performed with a TA Instruments TA 2000 Rheometer set to a 1% controlled strain mode, which was ensured to be within the linear viscoelastic regime. The measurements were performed with a parallel plate geometry of 25 mm in the frequency range of 100–0.01 Hz. Dielectric relaxation spectroscopy (DRS) was performed on a Novocontrol Alpha-A high performance frequency analyzer (Novocontrol Technologies GmbH & Co.) operating in the frequency range 10^{-1}-10^6 Hz at room temperature. The diameter of the tested 1 mm thick samples was 25 mm. Electrical

breakdown strengths were measured on an in-house built device based on international standards. The polymer film (~150 µm) was slid between two spherical electrodes, and a stepwise increasing voltage was applied (50-100 V/step). Each sample was subjected to 12 breakdown measurements, and an average of these values was given as the breakdown strength of the sample. The gel fractions were determined using swelling experiments, where samples of all prepared films were swelled in chloroform at RT for 48 hours. The chloroform was replaced after 24 hours. The solvent was decanted and the films were washed several times. The samples were thereafter dried for 48 h to a constant weight in an ambient atmosphere. Gel fractions were calculated as the weight after extraction and drying (m_e) against the initial weight of the sample (m_0) as $W_{gel} = m_e / m_0$.

2.2 Syntheses

All reactions were carried out in a nitrogen atmosphere.

α,ω-Allyl-poly((azidopropyl)methylsiloxane-*co*-dimethylsiloxane) with a 1200 g mol^{-1} pre-polymer **Co-1**: **Co-1** was synthesized according to a recently published procedure[26,27] using 3-chloropropylmethyldimethoxysilane (7.23 g, 39.6 mmol), hydride-terminated dimethylsiloxane (1200 g mol^{-1}) (50 g, 41.7 mmol), tris(pentafluorophenyl)borane (2 mL, 0.04 M, 0.2 mol%), dimethoxydimethylsilane (19.4 g, 163 mmol), allyldimethylsilane (9.76 g, 97.4 mmol), NaN_3 (12.4 g, 191 mmol) and tetrabutylammonium azide (1.09 g, 3.82 mmol) to produce a slightly yellowish oil (50.0 g, 96.6 %). SEC (toluene): $\bar{M}_w \approx 23{,}000$ g mol^{-1}.

α,ω-Allyl-poly((azidopropyl)methylsiloxane-*co*-dimethylsiloxane) with a 580 g mol^{-1} pre-polymer **Co-2**: **Co-2** was synthesized according to a recently published procedure[26,27] using 3-chloropropylmethyldimethoxysilane (15 g, 82.1 mmol), hydride-terminated dimethylsiloxane (580 g mol^{-1}) (45.7 g, 78.8 mmol), tris(pentafluorophenyl)borane (4.2 mL, 0.04 M, 0.2 mol%), dimethoxydimethylsilane (39.6 g, 329.4 mmol), allyldimethylsilane (10.0 g, 100 mmol), NaN_3 (19.9 g, 306 mmol) and tetrabutylammonium azide (2.17 g, 7.64 mmol) to produce a slightly yellowish oil (51.0 g, 91.1 %). SEC (toluene): $\bar{M}_w \approx 23{,}000$ g mol^{-1}.

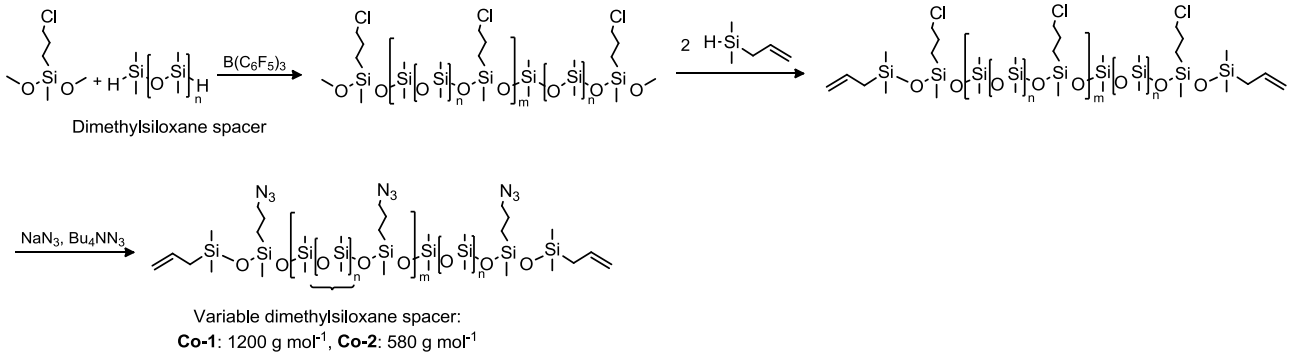
General procure for CuAAC, synthesis of α,ω-allyl-poly((4-(4-nitrophenyl)-1H-1,2,3-triazolepropyl)methylsiloxane-*co*-dimethylsiloxane) with a 1200 g mol^{-1} pre-polymer spacer: (**Co-1c**)
Co-1 (20 g, ~15.3 mmol (azidopropyl)methylsiloxane units) and 1-ethynyl-4-nitrobenzene (4.52 g, 30.7 mmol) were dissolved in dry THF (100 mL) in a 250 mL two-neck round bottom flask. CuI (0.29 g, 1.50 mmol) was subsequently added and Et_3N (2.33 g, 23.0 mmol) was added drop-wise. The reaction was carried out at 40°C for 17 hours at which point FTIR confirmed the disappearance of the azide band at 2095 cm^{-1}. THF was evaporated and the reaction mixture was precipitated into methanol. The solvent was decanted and the product was dried *in vacuo* giving a red viscous oil in quantitative yield.

Example of a partially functionalized copolymer: α,ω-allyl-poly((4-(4-nitrophenyl)-1*H*-1,2,3-triazolepropyl)methylsiloxane-*co*-(azidopropyl)methylsiloxane-*co*-dimethylsiloxane) with a 580 g mol^{-1} pre-polymer spacer (**Co-2a**):
The copolymer was prepared according to the general click reaction procedure using **Co-2** (10 g, ~13.7 mmol (azidopropyl)methylsiloxane units), 1-ethynyl-4-nitrobenzene (0.50 g, 3.4 mmol), CuI (0.07 g, 0.34 mmol) and Et_3N (0.52 g, 5.0 mmol) to produce a brown viscous oil in quantitative yield.

General procedure for elastomer synthesis:
Co-1, **Co-2** or vinyl-terminated PDMS ($\bar{M}_w \approx 25{,}000$ g mol$^{-1,}$ Sigma-Aldrich) (2.33 g, 10.1 mmol) and an 8-functional cross-linker (HMS-301, 0.066 g, 0.034 mmol) were mixed with treated silica particles (20 wt%) and the mixture was treated on a FlackTek Inc. DAC 150.1 FVZ-K SpeedMixer™. The catalyst (511) (20-100 ppm) was added thereafter and the mixture was speed-mixed once more. The mixture was the poured into 1 mm thick steel molds and furthermore coated as 150 µm films on a glass substrate and cured at 115°C.

3. RESULTS AND DISCUSSION

Functionalizable siloxane copolymers were prepared according to a previously described procedure[26,27] and as illustrated in Scheme 1.



Scheme 1. Synthetic route for functionalizable siloxane copolymers via borane catalyzed polycondensation.

The synthesis of siloxane copolymers with spatially well-distributed functional groups was accomplished through the tris(pentafluorophenyl)borane-catalyzed Piers-Rubinsztajn reaction of 3-chloropropylmethyldimethoxysilane and hydride-terminated dimethylsiloxane pre-polymers that act as spacer units between the functional groups. In this step methoxy-terminated copolymers are formed. The tris(pentafluorophenyl)borane-catalyzed polycondensation of hydrosilanes and methoxysilanes involves cleaving C-O and Si-H bonds while forming Si-O and C-H bonds in an exothermic reaction ($\Delta H \approx -250$ KJ/mol)[28]. The reaction is performed at room temperature using low levels of $B(C_6F_5)_3$ catalyst (0.2 mol%). Furthermore, high yields were obtained (> 95%). Two kinds of copolymers were prepared: One copolymer was prepared with a 1200 g mol^{-1} dimethylsiloxane spacer unit between the functional groups (**Co-1**) and the other copolymer was prepared with a 580 g mol^{-1} dimethylsiloxane spacer unit between the functional groups (**Co-2**). During the synthesis of the two copolymers similar molecular weights were targeted. The copolymer with the shorter spacer thus contains roughly double the amount of functional groups than the copolymer with the long spacer (at comparable copolymer molecular weights).

Subsequent end-functionalization of the copolymers with allyl-groups allow for hydrosilylation cross-linking reactions with hydride-functional cross-linker molecules.

Converting the methoxy end-groups to vinyl/allyl end-groups did not alter the molecular weight of the copolymers, as illustrated in the SEC traces presented in Figure 1.

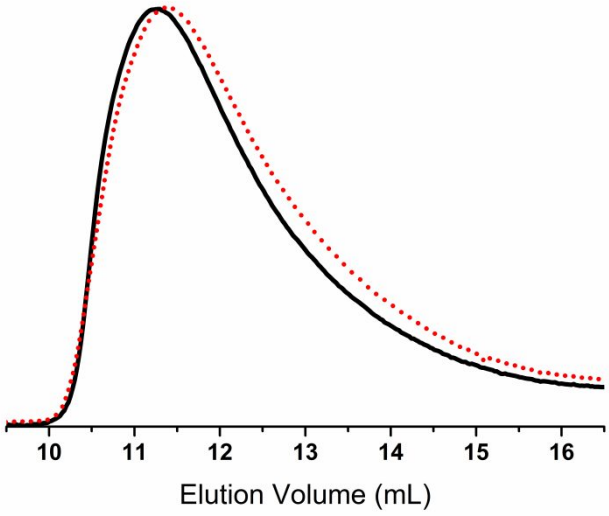
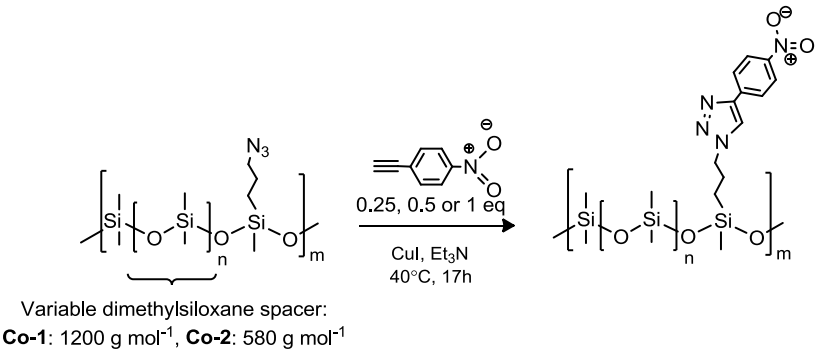


Figure 1. An overlay of the RI SEC traces of methoxy end-functional copolymer (black, ——) and vinyl end-functional copolymer (red, • • •).

The synthesized chloro-functional copolymers were converted to azido-functional through nucleophilic substitution in THF, using tetrabutylammonium azide as a phase-transfer catalyst as seen in Scheme 1. The azido-groups allow for attachment of high dielectric constant molecules through CuAAC click reactions. The molecular weights of the copolymers were analyzed with SEC using toluene as eluent, and molar mass characteristics were calculated from linear polydimethylsiloxane standards. The molecular weights of the copolymers prepared with different spacers were both found to be $\bar{M}_w \approx 23{,}000$ g mol^{-1}, which is a suitable molecular weight for silicone elastomers, as good mechanical properties are obtained for polymers of 20,000 to 30,000 g mol^{-1}.[29] **Co-1** and **Co-2** thus contain approximately 15 and 30 azido-groups, respectively.

The azido-functional copolymers, **Co-1** and **Co-2**, were thereafter functionalized with 1-ethynyl-4-nitrobenzene, through CuAAC, as illustrated in Scheme 2.



Scheme 2. Synthetic route to nitrobenzene-functionalized copolymers through CuAAC click reaction. The azido-functional copolymers are reacted with 0.25, 0.5 or 1 equivalents of 1-ethynyl-4-nitrobenzene to the total number of azido-groups.

The azido-groups on **Co-1** and **Co-2** were reacted to different extents (0.25, 0.5 or 1 equivalent of 1-ethynyl-4-nitrobenzene to the total number of azido-groups) so that copolymers with different degrees of dipolar functionalization were obtained. The efficiency of the CuAAC reaction allowed for direct control over the degree of functionalization from the feed of 1-ethynyl-4-nitrobenzene and the obtained degree of functionalization was determined through ^{1}H-NMR. The results are shown in Table 1.

Table 1. Overview of the prepared functionalized dipolar copolymers.

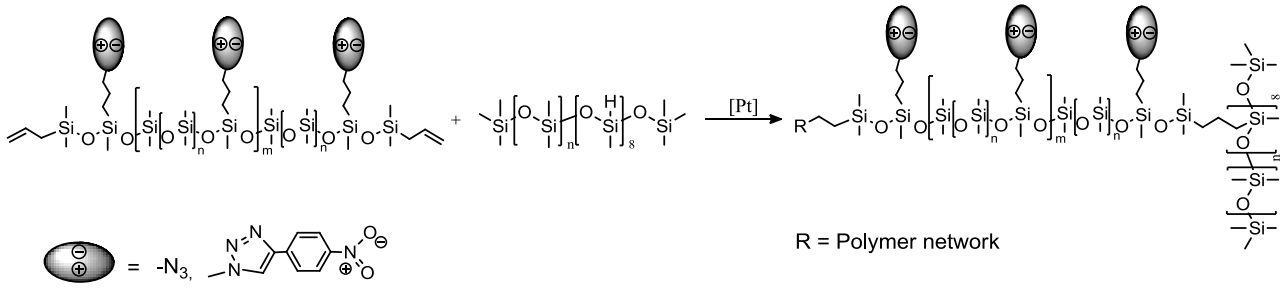
Entry	$\bar{M}_w$ dimethyl siloxane spacer [g mol^{-1}]	Feed of 1-ethynyl-4-nitrobenzene [% of azido-groups]	Degree of functionalization from ^{1}H-NMR [% of azido-groups]	Content of nitrobenzene [wt%]
Co-1	1200	0	0	0
Co-1a	1200	25	25	2.75
Co-1b	1200	50	51	5.6
Co-1c	1200	100	100	11
Co-2	580	0	0	0
Co-2a	580	25	19	3.8
Co-2b	580	50	42	8.4
Co-2c	580	100	100	20

The obtained degrees of nitrobenzene-functionalization were determined through the integration of the CH_2-N$_3$ resonance at δ_H = 3.23 ppm against the CH_2-N$_{triazole}$ resonance at δ_H = 4.41 ppm.

For **Co-1a-c** the feed of 1-ethynyl-4-nitrobenzene perfectly matched the obtained degree of functionalization determined from ^{1}H-NMR. This means, for example, that **Co-1a**, which was reacted with 0.25 equivalents of 1-ethynyl-4-nitrobenzene, had an integral of 0.75 for the CH_2-N$_3$ resonance and an integral of 0.25 for the CH_2-N$_{triazole}$ resonance. **Co-**

2a and **Co-2b** had slightly lower degrees of functionalization than what was aimed for with the 1-ethynyl-4-nitrobenzene feed. This could simply be due to inaccuracies when measuring the feed of 1-ethynyl-4-nitrobenzene during the CuAAC reactions. Overall, the degree of functionalization could be varied accurately by changing the 1-ethynyl-4-nitrobenzene feed and the corresponding obtained content of nitrobenzene is shown in Table 1.

Dipolar copolymers were reacted with 8-functional hydride cross-linkers as shown in Scheme 3 and furthermore reinforced with 20 wt% surface-treated silica particles.



Scheme 3. Cross-linking reaction between dipolar copolymers and a hydride-functional cross-linker.

A reference sample prepared from vinyl-terminated PDMS of $\bar{M}_w$ = 25,000 g mol^{-1} under similar reaction conditions (same cross-linker and particle concentration) was also produced.

The elastomers prepared with dipolar copolymers were characterized by FTIR and the spectra are shown in Figure 2.

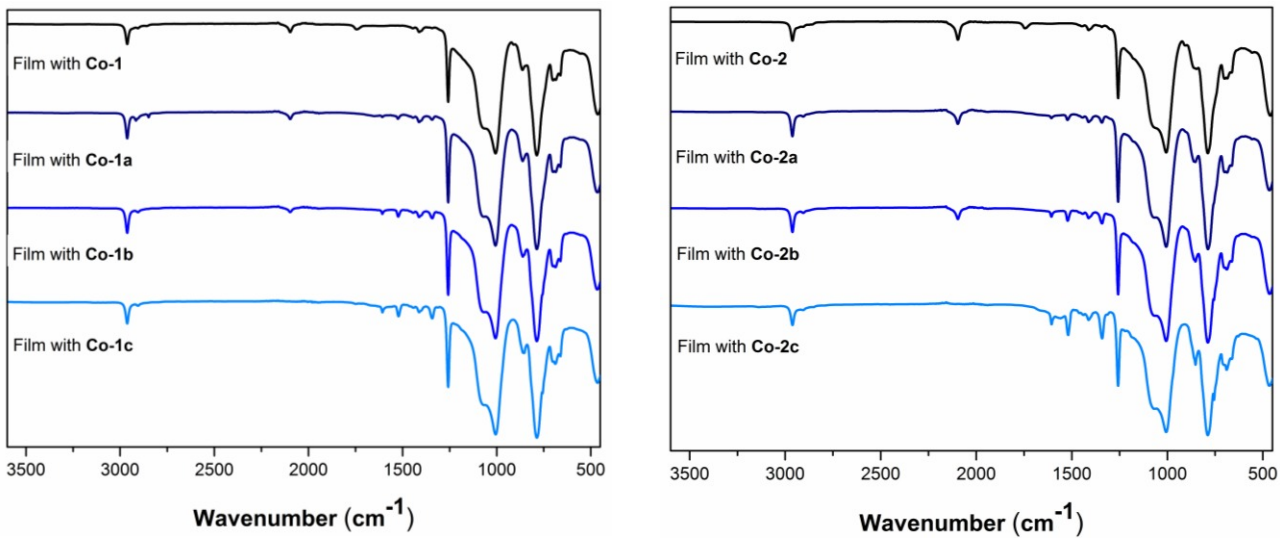


Figure 2. FTIR spectra of elastomer films prepared with the different functionalized copolymers: a): films prepared with copolymers with a 1200 g mol^{-1} pre-polymer spacer (**Co-1**) and b): films prepared with copolymers with a 580 g mol^{-1} pre-polymer spacer (**Co-2**).

The films with **Co-1** and **Co-2** (azido-functional copolymers), show distinctive –N_3 bands at ~2095 cm^{-1} and this band is sharper for **Co-2** due to the higher content of alkyl azide units on this copolymer compared to **Co-1**. The more reacted the azido-groups have become with 1-ethynyl-4-nitrobenzene, the less intense the –N_3 bands become, as evident from the spectra of **Co-1a-c** and **Co-2a-c**. For the films containing copolymer where all azido-groups have been reacted with 1-ethynyl-4-nitrobenzene no –N_3 are visible (film with **Co-1c** and **Co-2c**). All films prepared with 1-ethynyl-4-nitrobenzene containing copolymers (**Co-1a-c** and **Co-2a-c**) have spectra with bands of increasing intensity ~1605 cm^{-1} for the aromatic C=C bonds and at ~1520 cm^{-1} and ~1340 cm^{-1} for the N=O bonds with increasing 1-ethynyl-4-nitrobenzene content. This corroborates the increasing degree of functionalization with 1-ethynyl-4-nitrobenzene in the elastomers.

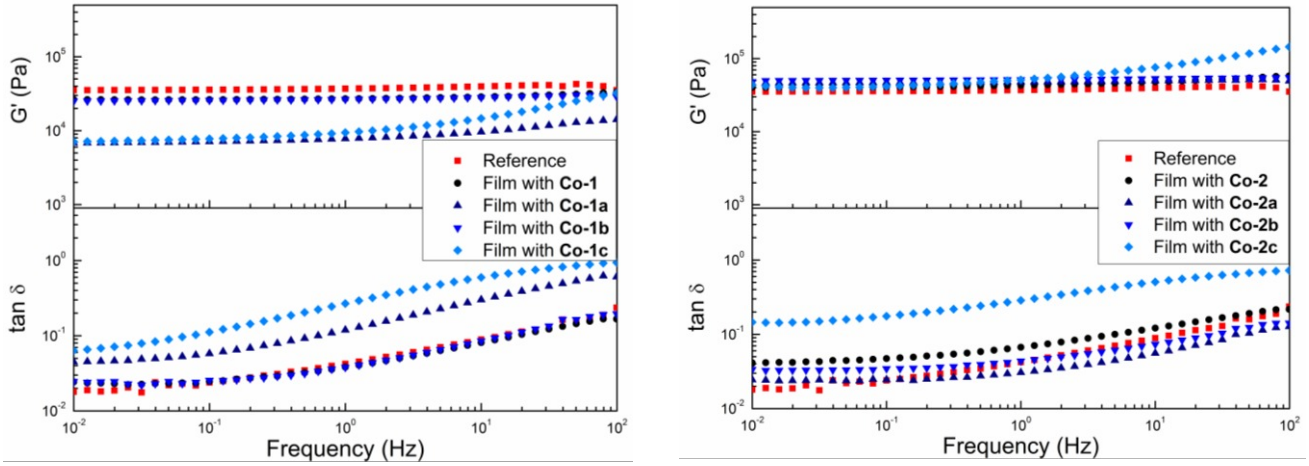
In order to elucidate the amount of bonded (gel fraction) and non-bonded (sol fraction) species in the elastomers, the gel fractions of the films were determined from swelling experiments with chloroform. This reveals how well cross-linked the elastomers are and thereby the mechanical integrity of the elastomer networks can be elucidated. The results of the gel fraction measurements are shown in Table 2.

Table 2: Gel fractions (W_{gel}) as a result of swelling experiments.

Film with entry	W_{gel} [%]
Ref.	97
Co-1	83
Co-1a	95
Co-1b	84
Co-1c	64
Co-2	84
Co-2a	97
Co-2b	88
Co-2c	69

The gel fractions are seen to decrease with increasing degree of functionalization of the azido-groups and the lowest gel fractions are obtained for films prepared with **Co-1c** and **Co-2c**. This could be due to the large content of 1-ethynyl-4-nitrobenzene which inhibits curing to some extent. The gel fractions for the other elastomers are, however, within an acceptable limit and these films are therefore better cross-linked.

The mechanical properties of the films prepared with the functionalized copolymers were investigated by linear rheology where the shear storage and shear loss moduli were determined. The resulting shear storage moduli (G') and loss (tan δ) are shown in Figure 3 and furthermore summarized in Table 3.



a) **b)**

Figure 3. Storage modulus (G') and loss (tan δ) as functions of frequency for: a): films prepared with copolymers with a 1200 g mol^{-1} pre-polymer spacer (**Co-1**) and b): films prepared with copolymers with a 580 g mol^{-1} pre-polymer spacer (**Co-2**).

It can be seen in Figure 3 that the films prepared with copolymers with the 1200 g mol^{-1} dimethylsiloxane spacer unit (**Co-1**) have lower storage moduli than the PDMS reference film. The films prepared with copolymers with the shorter dimethylsiloxane spacer unit (580 g mol^{-1}, **Co-2**) have comparable, but slightly higher, storage moduli – as for the reference film. Viscous losses (tan δ) remain low for all films expect for those prepared with copolymers with the highest concentration of 1-ethynyl-4-nitrobenzene (**Co-1c** and **Co-2c**). For these films the viscous losses increased six-fold, indicating increased damping behavior, which is partly or fully due to the larger fractions of extractable substructures[30].

The dielectric properties of the elastomers were investigated by dielectric relaxation spectroscopy and the resulting dielectric permittivity (ε') and dielectric loss (tan δ) spectra are shown in Figure 4 and furthermore summarized in Table 3. Enlarged spectra of dielectric permittivity at the plateau region from 10^2 to 10^5 Hz are also shown in Figure 4.

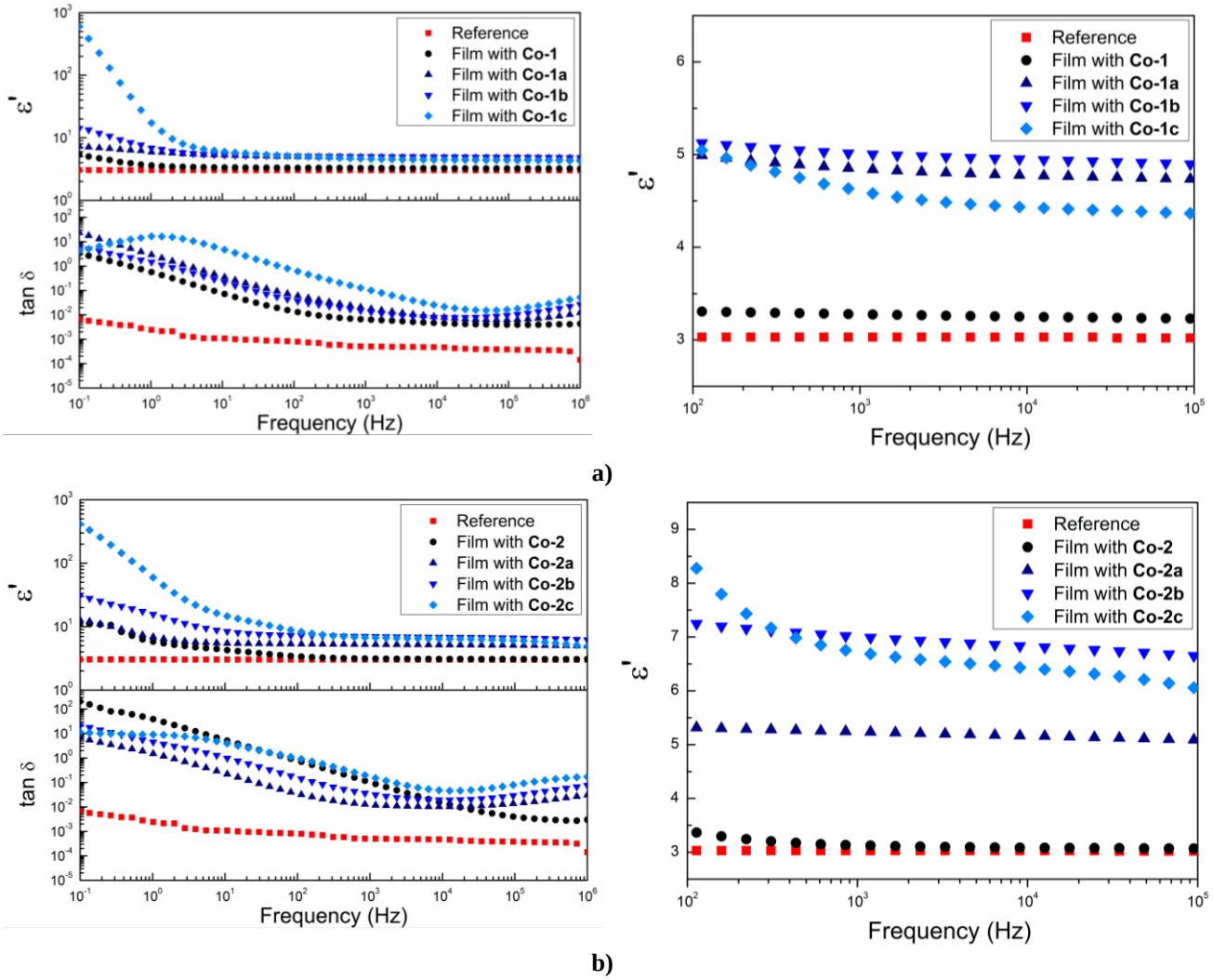


Figure 4. Dielectric permittivity (ε') and loss tangent (tan δ) as functions of frequency for films prepared with: a): films prepared with copolymers with a 1200 g mol^{-1} pre-polymer spacer (**Co-1**) and b): films prepared with copolymers with a 580 g mol^{-1} pre-polymer spacer (**Co-2**).

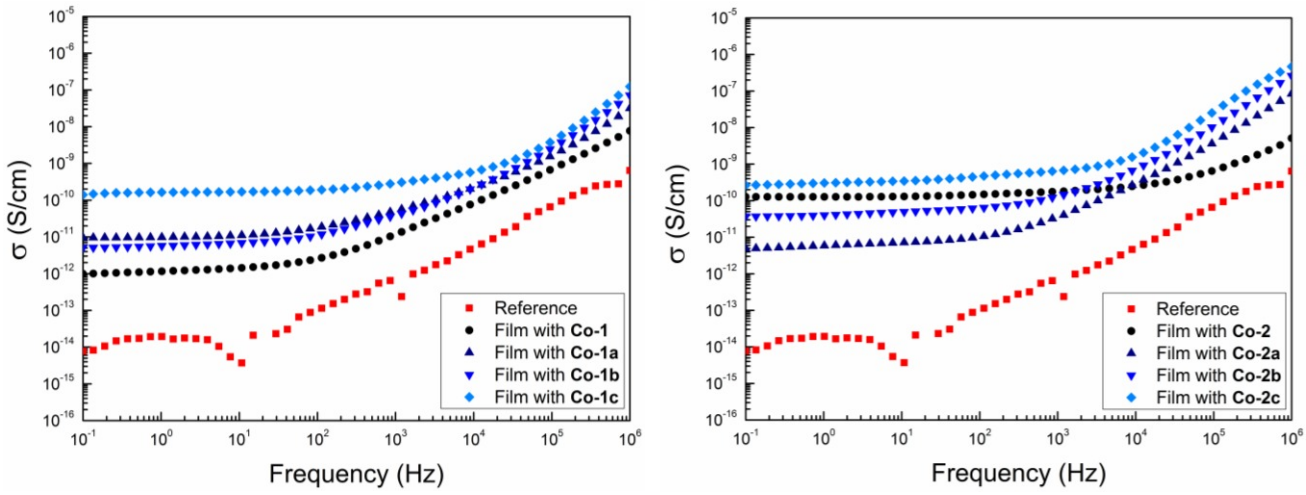
The dielectric permittivity is seen to increase for all films prepared with functional copolymers compared to the reference film for which ε' = 3.0. The films prepared with azido-functional copolymers (**Co-1** and **Co-2**) both show increased dielectric permittivity to ε' = 3.3 and ε' = 3.4 at 100 Hz, respectively, which corresponds to a 10-13% increase. This means that the doubling of alkyl azido-units from **Co-1** to **Co-2** does not increase the dielectric permittivity at medium to high frequencies. The film prepared with **Co-2** does, however, have higher dielectric permittivity at lower frequencies. Thus at 1 Hz, for instance, the dielectric permittivity has increased to ε' = 5.8 corresponding to an almost two-fold increase compared to the PDMS reference. These results mean that the azido-functional copolymers alone do also increase the dielectric permittivity of silicone elastomers, however, the dielectric loss, tan δ, has also increased, especially for the films prepared with **Co-2**.

Films prepared with copolymers with the long dimethylsiloxane spacer unit of 1200 g mol^{-1} and varying content of 1-ethynyl-4-nitrobenzene (**Co-1a-c**) show increased dielectric permittivity in the same order of magnitude (ε' ≈ 5) at 100 Hz, which correspond to an increase of ~70%. At lower frequencies dielectric permittivity increases in line with the increased content of 1-ethynyl-4-nitrobenzene, reaching ε' = 17.3 at 1 Hz for the film prepared with **Co-1c**, which contains 11 wt% 1-ethynyl-4-nitrobenzene. Dielectric losses, tan δ, increase somewhat in line with increasing 1-ethynyl-4-nitrobenzene content.

Elastomer films prepared with copolymers with the shorter dimethylsiloxane spacer unit, 580 g mol^{-1}, and varying content of 1-ethynyl-4-nitrobenzene (**Co-2a-c**), have high dielectric permittivities at 100 Hz, where the highest dielectric permittivity is obtained for the film prepared with **Co-2c** for which ε' = 8.5. This film contains 20 wt% 1-ethynyl-4-nitrobenzene and the increase in dielectric permittivity corresponds to an increase of 180% compared to the PDMS reference film. At frequencies higher than 100 Hz the film prepared with **Co-2b** shows the highest dielectric permittivity of ε' ≈ 7, whereas at lower frequencies the dielectric permittivity increase in line with increasing content of 1-ethynyl-4-nitrobenzene and reaches ε' = 59.3 at 1 Hz for the film prepared with **Co-2c**. Furthermore, dielectric losses (tan δ), increase in line with increasing content of 1-ethynyl-4-nitrobenzene but remain lower than that for the film prepared with the corresponding azido-functional copolymer **Co-2**.

In the medium to high frequency region (10^2-10^6 Hz), where the dielectric response depends mainly on bulk polarization processes[31], there are no significant changes in dielectric permittivity with frequency. Therefore, the most usable increases in permittivity for DE applications are observed in this frequency region. The largest increases in the dielectric permittivity are, remarkably, not necessarily observed for the films prepared with the copolymers with the highest content of 1-ethynyl-4-nitrobenzene and this indicates that there is a maximum concentration of functional 1-ethynyl-4-nitrobenzene groups above which further improvement to dielectric permittivity is not possible. Above this concentration, it is only permittivity at low frequencies (due to Maxwell polarization) and dielectric losses that increases. The tunable nature of this elastomer system makes it possible to specify the concentration and distribution of functional groups, and so it is possible to obtain the most optimal DE with regards to permittivity and dielectric loss.

Another important property for DE materials is the conductivity. Although silicone elastomers in general are electrically insulating materials (though no material can be considered as ideally insulating), upon changing of the molecular structure of the elastomer or adding high dielectric constant fillers, unwanted conductive paths – and thereby charge transport – can occur in the elastomer. Increased conductivity can lead to large dielectric losses and when conducting paths are created in an elastomer, the conductivity, σ, becomes independent of frequency below a critical frequency. Plots of the conductivity as function of frequency of the prepared functional elastomers are shown in Figure 5.



a) **b)**

Figure 5. Conductivity as a function of frequency for films prepared with: a): films prepared with copolymers with a 1200 g mol^{-1} pre-polymer spacer (**Co-1**) and b): films prepared with copolymers with a 580 g mol^{-1} pre-polymer spacer (**Co-2**).

It can be seen from Figure 5 that all films, including the PDMS reference film, show some conductivity at low frequencies, as conductivity becomes independent of frequency. The observed conductivities for all films, however, remain very low. For the films prepared from the copolymers with the highest content of 1-ethynyl-4-nitrobenzene (**Co-1c** and **Co-2c**) slightly higher conductivities are observed, which could be the reason for the high dielectric losses of these films at low frequencies.

The driving voltage that can be applied to a dielectric elastomer is limited upwards by the dielectric breakdown strength, E_B, which ideally is a material-specific constant. High dielectric breakdown strength is desired so that the DE does not experience premature failure. This means that it is important for the elastomer to be free from impurities or voids that cause locally reduced dielectric strength. The electrical breakdown strengths for films prepared with functional copolymers as well as the reference film are presented in Table 3.

Table 3. Dielectric permittivity (ε') and loss tangent (tan δ) at 1 Hz and 100 Hz as well as the breakdown strength (E_B), storage moduli (G') and loss (tan δ) and figure of merit calculated at 100 Hz for films with functional copolymers and the PDMS reference.

	Dielectric spectroscopy				Electrical breakdown	Rheology		Figure of merit
Film with entry	**ε′ @1Hz**	**ε′ @100Hz**	**tan δ @1Hz**	**tan δ @100Hz**	E_B **[V/µm]**	**G' @1Hz [kPa]**	**tan δ @1Hz**	F_{om}/F_{om_ref}
Ref.	3.0	3.0	0.002	0.0008	55.4	37.0	0.042	1.0
Co-1	3.6	3.3	0.56	0.01	61.4	27.0	0.038	1.9
Co-1a	5.9	5.0	2.90	0.06	63.2	7.81	0.119	10.3
Co-1b	6.9	5.1	1.47	0.04	69.2	26.5	0.038	3.7
Co-1c	17.3	5.0	16.7	0.60	60.5	9.41	0.268	7.8
Co-2	5.8	3.4	38.7	0.70	81.1	43.1	0.067	2.1
Co-2a	6.9	5.3	1.51	0.03	66.7	47.9	0.031	1.8
Co-2b	15.6	7.3	4.52	0.15	64.1	51.5	0.044	2.3
Co-2c	59.3	8.5	9.07	0.90	65.0	51.3	0.286	1.8

The electrical breakdown strength increases for all functional elastomer films compared to the PDMS reference film. This suggests that the use of the new functional copolymers for DEs does not compromise the dielectric breakdown strength, even though some of the films are softer than the reference film. A reduction in elastic modulus is often the reason for reduced electrical breakdown strength due to electromechanical instability[32].

The enhancement in the properties of the dipolar elastomers can be compared with the PDMS reference material by calculating the figure of merit, F_{om}, relative to the figure of merit for the reference film[20,33]. The figure of merit is a universal expression defined by Sommer-Larsen and Larsen[33], which, through a single parameter, can be used to evaluate the performance of a DE (at a constant potential). The figure of merit depends on the dielectric constant, dielectric breakdown strength and the Young's modulus (Y = 3G') of the elastomer material and it is defined as:

$$F_{om} = \frac{3\varepsilon' \cdot {E_B}^2}{Y} = \frac{\varepsilon' \cdot {E_B}^2}{G'}$$

The calculated figure of merit results are shown in Table 3 (calculated for results at 100 Hz). All films prepared with functional copolymers show increased F_{om}. The largest increase in the figure of merit is obtained for the film with the 1-ethynyl-4-nitrobenzene-functional copolymer **Co-1a** where the figure of merit is increased 10 times compared to the reference film. The high figure of merit of this film is among other things obtained because of its low modulus. The viscous and dielectric losses, however, are not incorporated into the figure of merit calculations but are important parameters that need to be considered. Therefore, when considering the losses, the best overall properties were obtained for a film prepared with a copolymer with a ~1200 g mol^{-1} dimethylsiloxane spacer and 5.6 wt% 1-ethynyl-4-nitrobenzene (**Co-1b**), as it has high dielectric permittivity (~70% increase at 100 Hz) and low dielectric loss. Furthermore, the obtained film was soft with low modulus, without compromising the viscous loss and gel fraction. Electrical breakdown strength also increased 25% compared to that of the pure PDMS reference film.

Moreover, the best overall properties were obtained for the films prepared with copolymers with the ~1200 gmol^{-1} pre-polymer spacer (**Co-1**), as the films prepared with copolymers with a shorter dimethylsiloxane spacer (~580 g mol^{-1}) and a higher concentration of functional groups (**Co-2**) were slightly stiffer and therefore less extensible.

4. CONCLUSION

A new high dielectric permittivity elastomer system was prepared through the use of dipolar siloxane copolymers. The copolymers were prepared with two different dimethylsiloxane spacer units between the functional groups. The siloxane copolymers were functionalized to various extents with the dipolar molecule 1-ethynyl-4-nitrobenzene through CuAAC reactions. ^{1}H-NMR corroborated the highly efficient functionalization reactions, and the degree of functionalization could thus be controlled directly from the 1-ethynyl-4-nitrobenzene feed. High dielectric permittivities were obtained for the 1-ethynyl-4-nitrobenzene-functional copolymers (e.g. a 180% increase at 20 wt% of 1-ethynyl-4-nitrobenzene), but this concentration resulted in an increase in dielectric loss and stiffness. The best overall properties were obtained for a film prepared with a copolymer with the longer dimethylsiloxane spacer unit and 5.6 wt% 1-ethynyl-4-nitrobenzene, as it had high dielectric permittivity (~70% increase at 100 Hz) and low dielectric loss. Furthermore, the obtained elastomer was soft, without compromising the viscous loss and gel fraction. Electrical breakdown strength for the elastomer with this degree of functionalization also increased 25% compared to that of a pure PDMS reference film. Moreover, the best overall properties were obtained for the films prepared with copolymers with the longer (1200 g mol^{-1}) pre-polymer spacer, as the films prepared with copolymers with a shorter dimethylsiloxane spacer (580 g mol^{-1}) and a higher concentration of functional groups were slightly stiffer and therefore less extensible.

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